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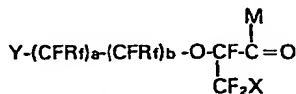
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(54) Preparation of novel vinyl ethers.

(57) The invention relates to a process to produce compounds represented by the general formula

$Y-(CFR_1)_a-(CFR_1)_b-O-CF=CF_2$
by decarboxylation of compounds represented by the general formula



where a = 0-3;

b = 0-3;

provided a + b = 2 or 3;

Y = an acid derivative;

X = Cl, I or Br;

M = OR, F, Cl, Br, I, OA;

A = alkali metal, alkali earth metal, a quaternary nitrogen and hydrogen;

R¹ and R₁ are independently selected from the group consisting of F, Cl, perfluoroalkyls and fluorochloroalkyls

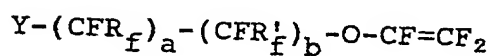
R = an alkyl having one or more carbon atoms or an aryl.

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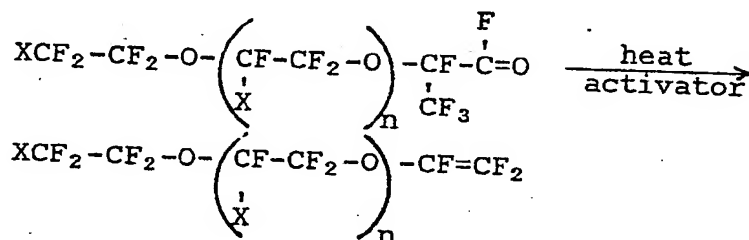
PREPARATION OF FLUORO VINYL ETHERS

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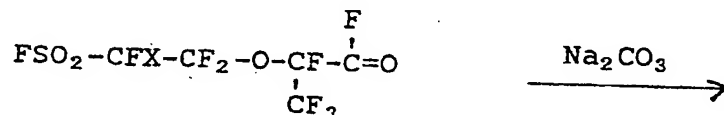
by decarboxylation.

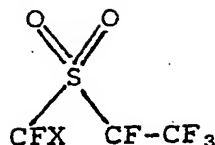
U.S. Patent 3,450,684 teaches the following reaction:



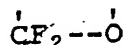
where X is F, Cl, H, CF_2H , CF_2Cl or CF_3
n is at least 1.

U.S. Patent 3,560,568 teaches the following reaction:





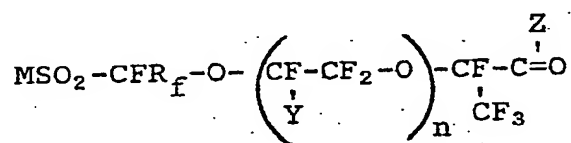
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where X is F or CF₃

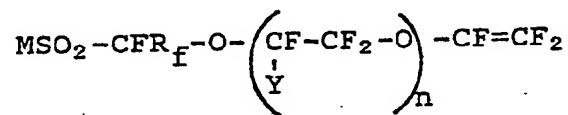
U.S. Patent 3,282,875 teaches that compounds represented by the general formula

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may be pyrolyzed at 200-600°C in the presence of a solid catalyst to compounds represented by the general formula

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where M is a radical selected from the group consisting of F, OH, amino, OMe

Me is an alkali metal radical, or a quaternary ammonium radical

Z is F or OX

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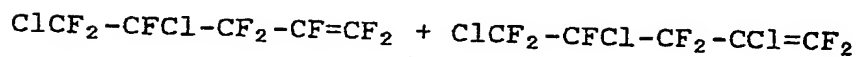
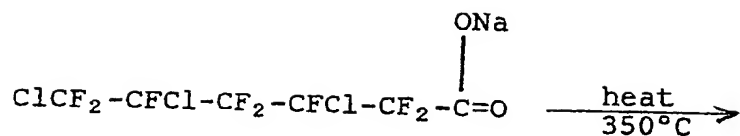
X is an alkali metal

Y is F or CF₃

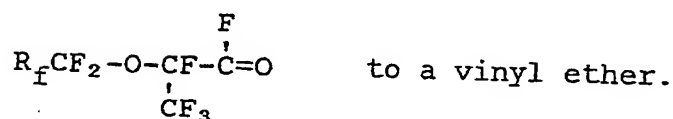
n is 1 to 3

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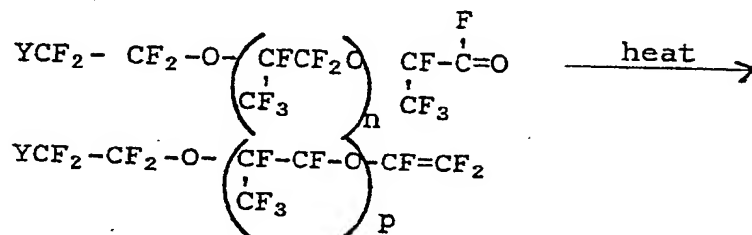
J. E. Fearn, et al teach in the Journal of Polymer Science, Vol. 4, Part A-1, p. 131-140, (1966) "Polymers and TerPolymers of Perfluoro-1,4,pentadiene, that in the pyrolysis of the sodium salts of carboxylic acids which contain fluorine and chlorine in the beta position, sodium chloride is preferentially, but not exclusively eliminated. For example



U.S. Patent 3,114,778 teaches the pyrolysis of



U.S. Patent 4,138,426 teaches the pyrolysis reaction



where Y is -COOR, -COOH, -COOM or -CN

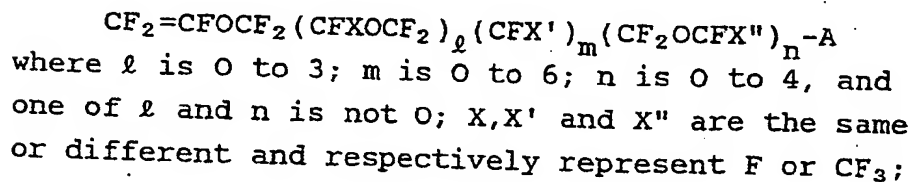
R is an alkyl group of from 1-6 carbon atoms

M is an alkali metal

p is 1 to 5

n is 1 to 6

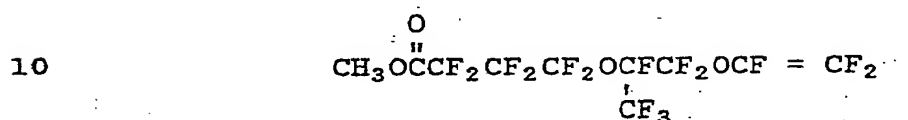
British Patent No. 1,518,387 teaches the use of polymers as membranes, from compounds represented by the structure



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A represents $-C\equiv N$, COF , $COOH$, $COOR_1$, $COOM$ and $CONR_2R_3$ and R_1 represents C_{1-10} alkyl group, R_2 and R_3 each represent a hydrogen atom or a C_{1-10} alkyl group and M represents an alkali metal or a quaternary ammonium group.

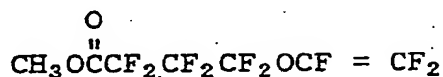
Compounds, such as



are shown as prepared by the addition of two equivalents of hexafluoropropylene oxide to one equivalent of



followed by decarboxylation to the vinyl ether. Compounds derived from the addition of one equivalent of the epoxide such as



are excluded by the general structure shown above.

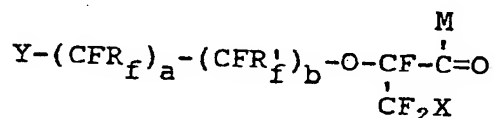
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R. D. Chambers, in his book, Fluorine in Organic Chemistry, published by John Wiley & Sons, 1973, pages 211-212, teaches that carboxylic acid derivatives may be converted to olefins. The conversion is taught to involve the loss of carbon dioxide and formation of an intermediate carbanion. The intermediate then loses NaF to form the resulting olefin.

Accordingly, the present invention resides in the discovery of compounds represented by the general formula



which are prepared by decarboxylation of compounds represented by the general formula



where a = 0-3

b = 0-3

provided a + b = 2 or 3

Y is an acid derivative

X = Cl, Br, or I

M = OR, F, Cl, Br, I or OA

A = alkali metal or quaternary nitrogen salt or hydrogen

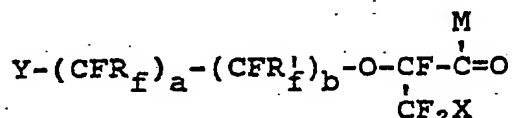
R_f' and R_f are independently selected from the group consisting of F, Cl, perfluoroalkyl and chlorofluoroalkyl radical

R is an alkyl group having one or more carbon atoms or an aryl.

The decarboxylation is carried out at a temperature from 50°C to 600°C, preferably from 80°C to 150°C, in the presence of an activator such as a base, ZnO, silica or other known activators.

Preferably, when R_f'; R_f and R is an alkyl or aryl radical, they have from 1 to 10, more preferably from 1 to 4, carbon atoms.

Based upon the known art, one would expect to produce cyclic compounds by decarboxylating compounds represented by the general formula

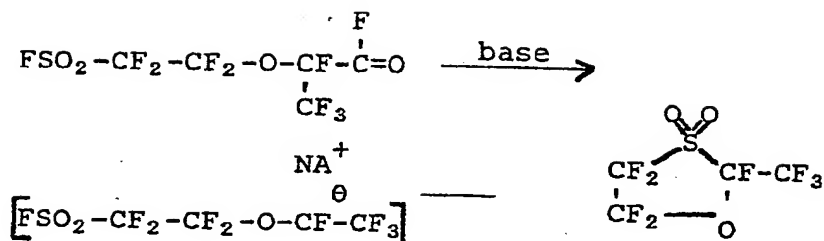


when Y is an acid derivative having a group displaceable by a nucleophile and when $a + b = 2$ or 3 .

This is the case as shown by U.S. 3,560,568 which shows ring formation when $Y = FSO_2$, $R_f = R'_f = F$, $X = F$ and $a + b = 2$.

It is generally accepted (see Chambers) that decarboxylations of acids or derivatives to olefins involves loss of carbon dioxide to form an intermediate carbanion. When Y contains a leaving group which can be displaced by a nucleophile, and $a + b = 2$ or 3 such that a 5 or 6 membered ring can be formed by displacing that leaving group from Y with the intermediate nucleophilic carbanion, then the 5 or 6 member ring would be the expected product. It is well known that because of the proximity of reactive groups involved in forming 5 or 6 membered rings and the stability of these rings, that formation of the rings is highly favored.

During the decarboxylation reaction of U.S. Patent 3,560,568 the following sequence is expected to occur which forms a reactive carbanion intermediate according to the following formula and then cyclizes to a cyclic sulfone from that intermediate.

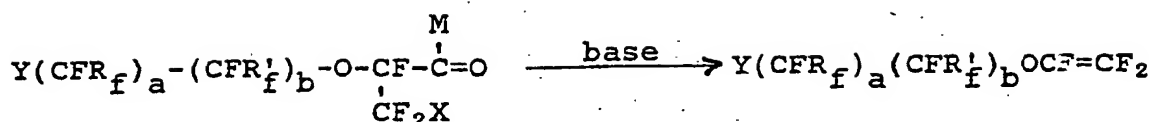


In this intermediate there is located a nucleophile (the carbanion) in a position such that formation of a 5 membered ring is possible by reaction of the carbanion with the sulfur, displacing F, to form NaF. This ring formation is shown by the patent and is confirmed by our comparative Example 1.

Ring formation is expected not only with FSO₂ but with other groups which fit the above description. For example, it is well known that carboxylic acid halides and phosphonic acid halides and esters readily react with nucleophiles such as OH⁻, or carbanions, such as methyl lithium, displacing the halide or alkoxide from the carbonyl or phosphoryl.

However, it has been unexpectedly found that a linear olefin results when X is Cl, I, or Br, as opposed to the prior art where X was F.

According to the present invention, the following compounds do not form rings during decarboxylation, although ring formation would be expected, but rather, they form linear, vinyl ether monomers useful in polymer synthesis, as shown by the following reaction:



where

a = 0-3

b = 0-3

provided a + b = 2 or 3,

Y is an acid derivative,

X = Cl, Br, I,

M = OR, F, Cl, Br, I or OA,

A = alkali metal, alkali earth metal,
quaternary nitrogen, or hydrogen;

R'_f and R_f are independently selected from
the group consisting of F, Cl, perfluoro-
alkyl and chlorofluoroalkyl,

R is an alkyl group having one or more
carbons or aryl.

Even though all ring-forming conditions are met, reaction site on Y for displacement and 5 or 6 membered ring formation, reaction occurs to produce the olefin substantially completely. Substantially complete formation of olefin, rather than cyclic compounds, by NaX elimination, particularly NaCl, is indeed surprising and unexpected.

The decarboxylation is conducted according to known methods, such as those taught by Chambers. For example, the decarboxylation temperatures may be from 50°C to 600°C, preferably from 80°C to 150°C and for a time sufficient to obtain substantial decarboxylation. The decarboxylation reaction may be conducted in the

presence of an activator. The activator may be a base such as sodium carbonate or ZnO, silica or other known activators.

Optionally, a dispersant may be used to enhance the decarboxylation reactions. Suitable dispersants should be unreactive and may include such materials as tetraglyme, diglyme or glyme.

It is particularly convenient to use a slurry of Na_2CO_3 in the above dispersants for the decarboxylation reactions.

In the general formula, Y is an acid derivative. For example, Y may be SO_2Z , $\text{P} = \text{O}$ or $\text{C} = \text{O}$ where Z is a leaving group such as OR, F, Cl, Br, or I and R is an alkyl radical having one or more carbon atoms or an aryl radical.

In the general formula, M may be OR, F, Cl, Br, I or OA where A is hydrogen, an alkali metal or a quaternary nitrogen and R is an alkyl radical having one or more carbon atoms or an aryl radical.

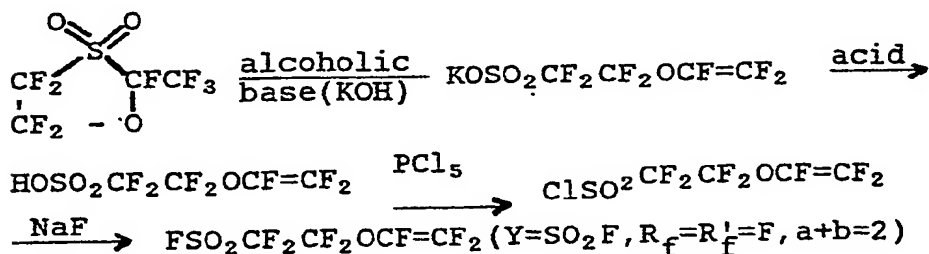
R_f and R'_f in the general formula, may be independently F, Cl or a perfluoroalkyl or a chloro-fluoroalkyl containing from one or more carbon atoms. a and b may independently represent an integer of 0 to 3, inclusive, provided that $a + b$ is equal to 2 or 3.

In addition to unexpectedly forming vinyl ether compounds rather than cyclic compounds, it is also surprising that there is not evidence of formation of X substituted olefins. In the decarboxylation

reaction either NaX can be eliminated to form $\sim\text{OCF}=\text{CF}_2$ or NaF can be eliminated to form $\sim\text{OCF}=\text{CFX}$. While it is not surprising that elimination of NaX predominates, it is surprising, particularly when $\text{X}=\text{Cl}$, to have substantially exclusive elimination of NaX. Fearn et al. reports the preferential elimination of chloride from pyrolysis of sodium salts of carboxylic acids which contain both fluorine and chlorine in the β position, but not exclusive elimination of chloride. Fearn et al. actually isolated some of the product resulting from fluoride elimination. No evidence, by I.R., Mass Spectroscopy or ^{19}F NMR, has shown indications of NaF elimination in the decarboxylation reactions of the present invention.

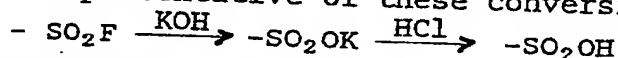
The discovery described herein represents a marked improvement over methods of the prior art for producing acid derivative functional vinyl ethers having three or four atoms, inclusive, between the functional group and the vinyl group. As discussed previously, formation of cyclic compounds resulted when decarboxylation reactions were used.

There is one reported method to prepare the compound $\text{FSO}_2\text{CF}_2\text{CF}_2\text{OCF}=\text{CF}_2$ (U.S. Patent 3,560,568). In this patent is taught the following sequence:



The cyclic sulfone starting material is prepared by decarboxylation of $\text{FSO}_2\text{CF}_2\text{CF}_2\text{OCFC}(\text{CF}_3)(\text{F})$ (Y=FSO₂, X=F, R_f=R'_f=F, a+b=2). Clearly, all of the steps shown by the above sequence are in addition to the reaction of the present invention. The same reaction as used for making the starting cyclic sulfone for the above sequence is the only reaction required for making the desired vinyl ether monomer in the present invention.

It is important to have the sulfonyl fluoride group in the vinyl ether monomer rather than having the sulfur present as sulfonic acid or the acid salt. Polymers and copolymers with other vinyl monomers made from the sulfonyl fluoride form of the monomer, and hence having the sulfonyl fluoride in the resulting polymers, are thermoplastic and can thus be fabricated into films, pellets and the like by conventional plastic fabrication techniques such as melt extrusion. Once fabricated, the polymers can then be hydrolyzed, with base, to the sodium salt of the acid which can then be easily converted to the sulfonic acid with a variety of commercial acids such as HCl, HNO₃, H₂SO₄, and the like. Representative of these conversions are:



These materials, in the acid and salt forms, are extremely useful as solid acid catalyst and ion exchange membranes, particularly as membranes in electrolytic chlor-alkali cells.

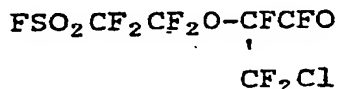
Preparation of the polymers with the monomer in the acid or salt form results in polymers with the functional group in the same form and renders the

polymers essentially unfabricatable by conventional fabrication techniques.

The above arguments apply equally well when $Y=COZ$ and $PO(Z)_2$. The fact that it is desirable to have Z equal halogen, OR or the like so that thermo-plastic polymers can be formed, fabricated and then easily converted to the acid or salt form means that Z must be a leaving group. Formation of the vinyl ether monomers by decarboxylation and having the properties provided by Z in the polymers as discussed above are mutually exclusive when $X=F$. The values provided for X in the present invention allow formation of the monomers by the one, simple, decarboxylation step and provide all of the desirable properties for the subsequently formed polymers.

Example 1

300 ml of dry tetraglyme and 62.2 grams anhydrous Na_2CO_3 were added to a 1000 ml 3 neck flask equipped with a magnetic stirrer, thermometer, reflux condenser and an inlet port. Two cold traps maintained at a temperature of $-78^\circ C$ were located in series downstream of the reflux condenser. 154 grams of product containing 92.1%



as identified by GCMS (Gas Chromatography-Mass Spectrophotometry) and VPC (Vapor Phase Chromatography) analyses were added dropwise. There was a slight temperature rise from $22^\circ C$ to about $35^\circ C$ over the period during the addition. The temperature of the reactor was increased

to 82°C. At this temperature there was obtained considerable reflux. The reflux condenser was removed and the product collected in the cold traps. The temperature was raised to 150°C with the system under vacuum. 80.5 gms of the product was collected in the first cold trap and 1 gm in the second trap. The product was analyzed by VPC and IR. Essentially all of the starting material had reacted. The yield to the $n=0$ product ($\text{FSO}_2\text{CF}_2\text{CF}_2\text{OCF}=\text{CF}_2$) was 70.6% as a product analyzing 95% $\text{FSO}_2\text{CF}_2\text{CF}_2\text{OCF}=\text{CF}_2$ by VPC. IR analysis showed bands as follows:

Vinyl Ether	-	1830	wave no. (cm^{-1})
- SO_2F	-	1460	" "
- SO_2F	-	1240	" "
- SF	-	810	" "

VPC

Boiling Point (B.P.) = 75°-76°C.

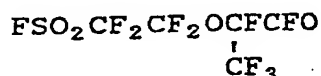
A direct titration of the unsaturation in the above product with Br_2 in CCl_4 was done to further confirm the structure. 20 ml of CCl_4 solution containing 2 gm Br_2 was made up as titrant. Two grams of the monomer was dissolved into 5 ml CCl_4 and titrated at ambient temperature to the point of color persistence. The titration required 10.9 ml of the bromine solution or 0.0068 moles of bromine. The apparent molecular weight of the monomer is then $\frac{2\text{gm}}{.0068}$ moles = 293.6 or a difference from the proposed structure of $\frac{293.6-280}{280} \times 100 = 5.4\%$. This value is in excellent agreement with the purity indicated by VPC analysis.

Comparative Example 1.

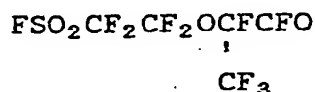
100 ml of tetraglyme and 9.84 gms anhydrous Na_2CO_3 were added to a 500 ml 3 neck flask equipped

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with a magnetic stirrer, thermometer, reflux condenser, and a dropping funnel. Two cold traps maintained at a temperature of -78°C , were located in series downstream of the reflux condenser. 29.35 grams of product analyzing at 84.4%



by VPC were added dropwise over a 3 hour period with evolution of CO_2 . The reflux condenser was removed. The reactor was heated to 78°C - 80°C while maintaining a slight N_2 sweep through the reactor to remove the product. 15.69 grams were recovered in the first cold trap and 0.6 grams in the second. The product was analyzed by VPC and IR. Conversion of the

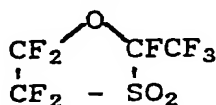


was essentially complete giving a yield of 77% to a product which was not a fluorosulfonylperfluoro vinyl ether. IR analysis showed bands as follows:

Wave No. (cm^{-1})	
1360	$\begin{array}{c} \cdot \text{O} \\ - \text{S} - \\ \text{O} \end{array}$
1150	$\begin{array}{c} \text{O} \\ - \text{S} - \\ \text{O} \end{array}$

B. Pt. $\sim 80^{\circ}\text{C}$.

The product was believed to be the sulfone



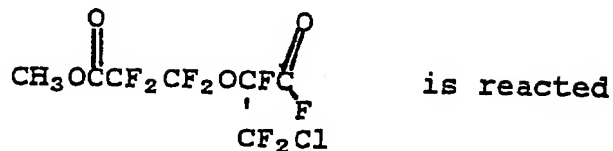
described in U.S. Patent 3,560,568.

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Example 2

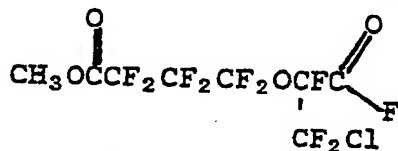
Using a procedure similar to Example 1,



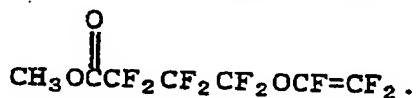
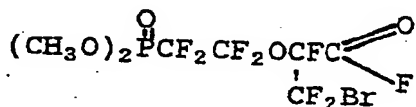
with a slurry of sodium carbonate in tetraglyme. After liberation of carbon dioxide, $\text{CH}_3\text{OCCF}_2\text{CF}_2\text{OCF}=\text{CF}_2$ is distilled from the reaction medium.

Example 3

By the same procedure as Example 2,



is decarboxylated to yield the vinyl ether

Example 4

is reacted with a slurry of sodium carbonate in tetraglyme using conditions as described in Example 1.

The linear vinyl ether, $(\text{CH}_3\text{O})_2\text{PCF}_2\text{CF}_2\text{OCF}=\text{CF}_2$, is distilled from the reaction medium.

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Example 5

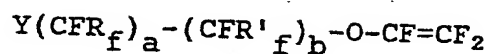
$$\text{FSO}_2\text{CF}_2\text{CF}_2\text{OCFC} \begin{array}{l} \text{O} \\ \parallel \\ \text{CF}_2\text{Cl} \end{array} \text{F}$$
 in methanol, is titrated with two equivalents of sodium hydroxide. Evaporation of the solvent gave, as a solid residue,

$$\text{FSO}_2\text{CF}_2\text{CF}_2\text{OCFC} \begin{array}{l} \text{O} \\ \parallel \\ \text{CF}_2\text{Cl} \end{array} \text{ONa},$$
 which was then pyrolyzed to give

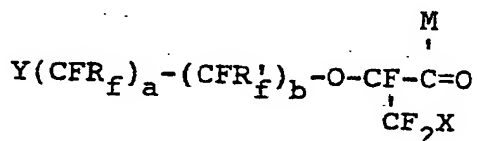
$$\text{FSO}_2\text{CF}_2\text{CF}_2\text{OCF}=\text{CF}_2.$$

CLAIMS

1. A method of preparing compositions represented by the general formula



which comprises decarboxylating



where X = Cl, I, or Br,

Y = an acid derivative,

R'_f and R_f are independently selected from the group consisting of F, Cl, perfluoroalkyl radicals and fluorochloro alkyl radicals,

a = 0-3,

b = 0-3,

a + b = 2 or 3,

M = OR, F, Cl, Br, I or OA,

A = an alkali metal, alkali earth metal, a quaternary nitrogen, and hydrogen,

R = an alkyl radical containing one or more carbon atoms or an aryl radical.

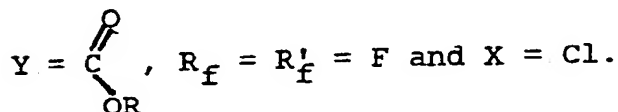
2. The method of Claim 1 wherein Y is selected from the group consisting of SO_2Z , $\text{P}=\text{O}$ and $\text{C}=\text{O}$, where

$$\begin{array}{ccc} & \text{Z} & \\ & | & \\ (\text{Z})_2 & & \text{Z} \end{array}$$

Z is OR, F, Cl, Br, or I.

3. The method of Claim 2 where Y is SO_2Z , $\text{Z} = \text{F}$, $\text{R}_f = \text{R}'_f = \text{F}$, and $\text{X} = \text{Cl}$.

4. The method of Claim 1 where



5. The method of Claim 1 where $\text{Y} = \text{PO}(\text{OR})_2$, $\text{R}_f = \text{R}'_f = \text{F}$.

6. The method of Claim 1 where $\text{Y} = \text{SO}_2\text{F}$, $\text{R}_f = \text{R}'_f = \text{F}$, $\text{X} = \text{Cl}$ and $a + b = 2$.

7. The method of any one of the preceding Claims wherein the method is carried out at a temperature of from 50°C to 600°C and for a time period of from 5 minutes to 10 hours.

8. The method of Claim 7, wherein the temperature is preferably from 80°C to 150°C and the time period is from 30 minutes to 4 hours.

9. The method of any one of the preceding Claims wherein the method is carried out in the presence of a base.

10. The method of any one of the preceding Claims wherein $\text{X} = \text{Cl}$.



European Patent
Office

EUROPEAN SEARCH REPORT

0041738

Application number

EP 81 10 4468

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	<u>FR - A - 1 341 087</u> (E.I. DU PONT DE NEMOURS) * abstract *	1	C 07 F 9/40 C 07 C 69/708 67/32 143/70 41/24
A	<u>FR - A - 1 410 444</u> (E.I. DU PONT DE NEMOURS) * abstract 1-3, 13 *	1	
A	<u>FR - A - 1 422 147</u> (E.I. DU PONT DE NEMOURS) * abstract 1-6 *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.)
			C 07 C 41/24 43/16 43/17 69/708 67/32 C 07 F 9/40
			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
			&: member of the same patent family, corresponding document
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 27-08-1981	Examiner SAGATYS

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